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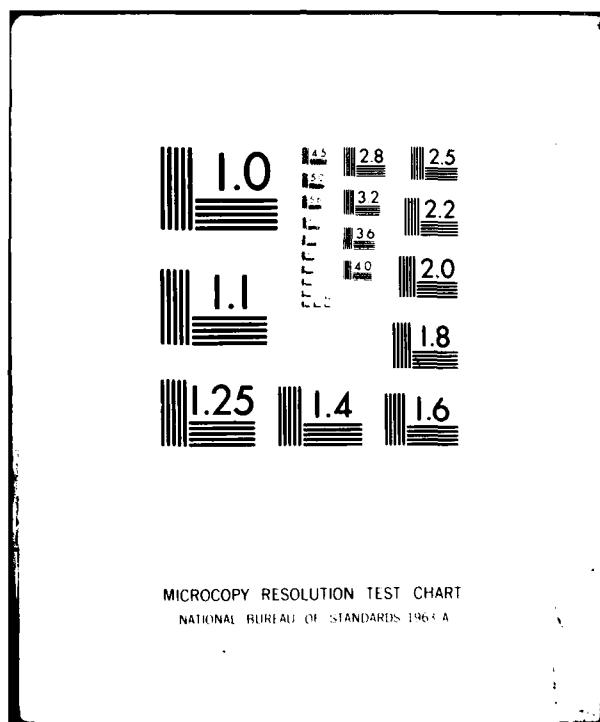
THE INTERFACIAL STRUCTURE OF A MIXTURE OF CHARGED HARD SPHERES --ETC(U)
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The Interfacial Structure of a Mixture of Charged
Hard Spheres and Dipolar Hard Spheres Near a
Charged Wall

by

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INTRODUCTION

In the past few years, there has been a renewed interest in the structure of an electrolyte at an electrode interface (the so-called electric double layer). If only the ions are taken into account explicitly, with the solvent represented by a uniform dielectric medium of constant dielectric constant ϵ , the potential difference across the double layer is much smaller than is observed experimentally. This remains true even if the Poisson-Boltzmann theory of Gouy¹ and Chapman² (GC) is replaced by more refined theories, such as the hypernetted chain approximation.^{3,4}

Presumably, this error is due to the simplified treatment of the solvent. If it is assumed that the dielectric constant $\bar{\epsilon}$ in the so-called inner region between the hard, flat, charged wall (the electrode) and a plane passing through the centers of the charged hard spheres in contact with the wall is different from the bulk value ϵ , the potential drop across the interface is

$$V = \frac{\sigma E}{2\bar{\epsilon}} + \phi_0. \quad (1)$$

where σ is the diameter of the charged hard spheres ($\sigma/2$ is then the distance of closest approach to the wall), $-E/4\pi$ is the charge density on the wall, and ϕ_0 is the potential difference between the plane of $\sigma/2$ and infinity, as shown in Fig. 1.

If $\bar{\epsilon} = \epsilon$, the calculated V is too small. Choosing $\bar{\epsilon} < \epsilon$ gives a larger potential difference. Obviously $\bar{\epsilon}$ can be adjusted to agree with experiment. The fact that a single value of $\bar{\epsilon}$ gives fairly good agreement with experiment for a wide range of concentrations and values of E indicates that there is a physical basis to this *ad hoc* procedure. However, as

will be shown, the view that the solvent structure need be taken into account only in a single layer is too extreme.

ION-DIPOLE MODEL

A more realistic model of the solvent is a collection of hard spheres with imbedded point dipoles. Although lacking as a model of water, it is certainly a better model solvent than a dielectric continuum with or without a discontinuity in the dielectric constant near the wall. Our model electrolyte is then a mixture of charged hard spheres of diameter σ and charge $z_i e$ (where z_i is the valence of ionic species i and e is the magnitude of the electronic charge) and dipolar hard spheres of diameter σ and dipole moment μ . We could consider the ions to be of different diameter. We will not do this firstly because there has been little theoretical work on the theory of ions of unequal size and secondly because, as we shall see, the explicit solvent term dominates and so the effect of differences in ionic diameters is small.

Let $\rho_i = N_i/V$ (V is the volume) be density of the ions of species i and $\rho_d = N_d/V$ be the density of the dipoles. Further, let

$$\rho_0 = \sum_i \rho_i . \quad (1)$$

Because of charge neutrality,

$$\sum_i p_i z_i = 0. \quad (2)$$

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Near the wall the electrolyte will be inhomogeneous. Thus, there is a density profile for the ions which we may write

$$\begin{aligned}\rho_i(x) &= \rho_i g_i(x) \\ &= \rho_i [h_i(x) + 1],\end{aligned}\quad (3)$$

where x is the distance from the wall. Similarly, the density profile of the dipoles is

$$\rho_d(x, \Omega) = \rho_d g_d(x, \Omega), \quad (4)$$

where Ω specifies the orientation of the dipoles. Now,

$$g_d(x, \Omega) = g_d^0(x) + \sqrt{3} \Delta h_d(x) \cos \theta + \dots, \quad (5)$$

where

$$\begin{aligned}g_d^0(x) &= 1 + h_d^0(x) \\ &= \frac{1}{4\pi} \int g_s(x, \Omega) d\Omega,\end{aligned}\quad (6)$$

where $d\Omega$ is the differential element of solid angle, and

$$\Delta h_d(x) = \frac{\sqrt{3}}{4\pi} \int g_d(x, \Omega) \cos \theta d\Omega, \quad (7)$$

where θ is measured from a normal from the wall.

If $-E/4\pi$ is the charge density on the wall, then the total amount of charge accumulated near the wall must be equal in magnitude, but opposite in sign to this charge

density. Hence,

$$e \sum_{i=1}^m z_i \rho_i \int_0^{\infty} h_i(t) dt = E/4\pi. \quad (8)$$

The potential difference across the interface is

$$V = 4\pi e \sum_{i=1}^m z_i \rho_i \int_0^{\infty} t h_i(t) dt$$

$$+ \frac{4\pi}{\sqrt{3}} \rho_d \mu \int_0^{\infty} \Delta h_d(t) dt,$$

where $\mu = |\mu|$.

THE MEAN SPHERICAL APPROXIMATION

Having specified the model and defined the relevant functions, an approximation must be introduced to obtain results. First, we use the mean spherical approximation (MSA) where the core condition $g(x)=0$ inside the ionic or solvent cores is combined with the approximation that outside the cores, the direct correlation function is equal to the negative of the pair potential divided by kT (k is Boltzmann's constant and T is the temperature).

The MSA integral equation has been solved for the ion-dipole-wall system.^{5,6} The general solution is implicit and has not yet been examined fully. However, in the limit of low concentrations of ions, the MSA results are explicit. In this low concentration limit,

$$g_i(x) = g_0(x) + \frac{\beta z_i e E}{e \kappa} e^{-\epsilon(x-a/2)}. \quad (10)$$

where $g_0(x)$ is the density profile (normalized) for hard spheres near a hard wall,⁷ $\beta = 1/kT$, and

$$\kappa^2 = \frac{4\pi\beta e^2}{\epsilon} \sum_{i=1}^m z_i^2 \rho_i, \quad (11)$$

is the Debye screening length.

Apart from the term $g_0(x)$, which makes no contribution in either Eq. (8) or (9) because of charge neutrality, Eq. (10) is the solution of the MSA for a system of charged hard spheres in a dielectric medium of dielectric constant ϵ . In other words, *at low concentrations in the MSA, the ionic terms have been decoupled from the dipolar terms.*

In the MSA, $g_d^0(x)$ is the hard sphere/hard wall profile, $g_0(x)$. In the limit of low concentrations, $\Delta h_d(x)$ satisfies

$$\begin{aligned} \Delta h_d(x) = & -\frac{4\pi}{3} \beta e \mu \frac{\beta_6^2}{\beta_3} \sum_i z_i \rho_i \left\{ \int_{x-s_{di}}^{\infty} h_i(t) dt \right. \\ & + \left[s_{di} + \frac{\beta_6^2}{4 \beta_3 \beta_{12}} \sigma_d \right] h_i(x - s_{di}) \\ & + \left. \left(\frac{\sigma_d}{2} \right) \frac{\beta_3}{\beta_{12}} \int_{s_{di}}^{(\sigma_d, x - \sigma_d/2)} \left(\frac{t - \sigma_{di}}{\sigma_d^2} \right) h_i(x - t - s_{di}) dt \right\} \\ & + b_2 \frac{\beta_3}{\beta_6^2} \int_0^{(\sigma_d, x - \sigma_d/2)} \left(\frac{t^2 - \sigma_d^2}{\sigma_d^2} \right) \Delta h_d(x - t) dt \\ & - 2b_2 \frac{\beta_3 - \beta_{12}}{\beta_6^2} \int_0^{(\sigma_d, x - \sigma_d/2)} \left(\frac{t - \sigma_d}{\sigma_d^2} \right) \Delta h_d(x - t) dt. \end{aligned} \quad (12)$$

where

$$s_{di} = \frac{\sigma_d - \sigma}{2}, \quad (13)$$

$$\sigma_{di} = \frac{\sigma_d + \sigma}{2},$$

(a,b) means that the minimum of a and b is to be used, and

$$\beta_{3 \cdot 2^n} = 1 + (-1)^n b_2 / (3 \cdot 2^n). \quad (15)$$

The parameter b_2 (and thus, β_3 , β_6 , and β_{12}) is related to ϵ by

$$\epsilon = \frac{\beta_{12}^4 \beta_3^2}{\beta_6^6}. \quad (14)$$

The MSA values for the two integrals which contribute to V in Eq. (9) are

$$4\pi e \sum_i z_i \rho_i \int_0^\infty t h_i(t) dt = \frac{E}{\kappa} \left[1 + \frac{\kappa \sigma}{2} \right] \quad (15)$$

and

$$\frac{4\pi}{\sqrt{3}} \rho_d \mu \int_0^\infty \Delta h_d(t) dt = \frac{1-\epsilon}{\epsilon} \left[1 + \frac{\kappa}{2} (\sigma - \sigma_d/\lambda) \right] \frac{E}{\kappa}, \quad (16)$$

where $\lambda = \beta_3/\beta_6$. Thus,

$$V + \frac{E}{\epsilon \kappa} \left[1 + \frac{\kappa}{2} \left(\sigma + \frac{\epsilon-1}{\lambda} \sigma_d \right) \right]. \quad (17)$$

It is to be noted that there has been a cancellation between terms of order 1 and $(\epsilon-1)/\epsilon$ to produce a term of order $1/\epsilon$. If

$$\sigma_d = 0,$$

we obtain

$$V = \frac{E}{\epsilon\kappa} \left[1 + \frac{\kappa\sigma}{2} \right], \quad (18)$$

which is the result for charged hard spheres in a uniform dielectric medium. Thus, the contribution due to the discrete nature of the solvent is $(\epsilon-1)\sigma_d E/2\lambda\epsilon$. This is *formally* identical to Eq. (1). In fact, if

$$\bar{\epsilon} = \frac{\epsilon}{1 + \frac{\epsilon-1}{\lambda} \left(\frac{\sigma_d}{\sigma} \right)}, \quad (19)$$

Eqs. (1) and (17) are identical (if the MSA is used to calculate ϕ_0). However, the underlying physical pictures are quite different. In Eq. (1), the solvent is presumed to be affected by the wall only within an inner layer of thickness $\sigma/2$ whereas, as is seen from Fig. 2, the orientational effects of the dipoles near the wall extend several layers into the blind. It is not meaningful to talk about an inner layer capacitor in series with a diffuse layer capacitor.

Equation (14) can be rewritten as

$$16\epsilon = \lambda^2(\lambda + 1)^4. \quad (20)$$

If ϵ is set equal to the bulk dielectric constant of water ($\epsilon \sim 78$), $\lambda = 2.65$. Thus, $(\epsilon-1)/\lambda = 29.1$. A reasonable value for water is $\sigma_d = 2.76 \text{ \AA}$. The solvent term $(\epsilon-1)\sigma_d/\lambda$ dominates so that the precise value used for σ is not critical. For simplicity, we may use

$\sigma = \sigma_d$. Results obtained from Eq. (17) for the differential capacitance,

$$C_d = \frac{1}{4\pi} \frac{\partial E}{\partial V}$$

$$= \frac{\epsilon}{4\pi} \frac{\kappa}{1 + \frac{\kappa}{2} \left(\sigma + \frac{\epsilon-1}{\lambda} \sigma_d \right)}, \quad (21)$$

compared with experiment⁸ in Table 1. In as much as the MSA is a linearized theory, it is expected to be useful only for small charge on the electrode. As a result, the comparison in Table 1 is confined to this region. The agreement is good considering that no adjustable parameters are employed.

A SIMPLE EXTENSION OF THE MSA

Well known extensions of the MSA exist. Examples are the hypernetted chain (HNC) approximation and more simple LHNC and QHNC approximations. The LHNC approximation is a linearized theory and presumably shares many of the deficiencies of the MSA. The others are more complex and lead to equations which are difficult to solve even numerically.

In addition to the numerical difficulties, there exists another problem. We have seen that in the MSA, there is a cancellation between terms of order 1 and $(\epsilon-1)/\epsilon$ to produce a term of order $1/\epsilon$ in the potential. This was no problem in the MSA since all the terms were analytic. However, in a theory where the analogues of Eqs. (15) and (16) are obtained numerically and where $\epsilon \sim 80$, a one percent error in either term may produce a hundred percent error in V. Clearly, a theory must be formulated so that this cancellation is effected

before the commencement of numerical calculations if a reliable result for V is to be obtained.

In the MSA, Eq. (12) is coupled with the solution of the MSA for $h_i(x)$ for charged hard spheres in a uniform continuum dielectric medium. A simple procedure would be to retain Eq. (12) but to use some more general expression for $h_i(x)$ such as the nonlinear GC theory or the HNC theory for charged hard spheres in a dielectric background.

In general, $h_i(x)$ would have to be determined numerically. However, as long as the $h_i(x)$ satisfy charge neutrality, Eq. (8), the potential is given by

$$V = \frac{4\pi e}{\epsilon} \sum_i z_i \rho_i \int_0^{\infty} t h_i(t) dt + \frac{\epsilon - 1}{\epsilon} \frac{E \sigma_d}{2\lambda} . \quad (22)$$

The desired cancellation between terms of order 1 and $(\epsilon - 1)/\epsilon$ has been accomplished.

Values for

$$\phi_0 = \frac{4\pi e}{\epsilon} \sum_i z_i \rho_i \int_{\sigma/2}^{\infty} (t - \sigma/2) h_i(t) dt , \quad (21)$$

calculated from the MSA, GC and HNC theories for charged hard spheres in a dielectric medium, are compared with the simulation results of Torrie and Valleau⁹ in Fig. 3. The MSA result is useful only for small charge densities on the wall. The GC theory results are appreciably larger than the simulation results. On the other hand, the HNC results are in quite good agreement with the simulation results.

For the total potential V , and thus the differential capacitance, the explicit solvent contribution, $(\epsilon-1)E\sigma_d/2\lambda\epsilon$, dominates. Hence, as is seen in Fig. 4, the differences in C_d between the use of the GC and HNC results for $h_i(x)$ in Eq. (21) are smaller.

SUMMARY

Equation (12) provides a theoretical basis for Eq. (1). The potential is *formally* identical that obtained from a collection of charged hard spheres in dielectric medium near a charged hard wall with an inner layer whose properties are different from the bulk. However, the physical interpretation is quite different. The effect of the wall on the solvent is not confined to an inner layer of thickness $\sigma/2$ but extends for several days into the fluid. In addition, no artificial semi-macroscopic concept, such as a local dielectric constant, need be introduced. The explicit solvent contribution to V arises from microscopic orientational effects on the dipoles near the wall.

The agreement with experiment is qualitative. To obtain better agreement with experiment $(\epsilon-1)/\lambda$ would have to be treated as a parameter. The charge in $(\epsilon-1)/\lambda$ would not be large and could be ascribed to polarization or some other phenomenon neglected in the model.

One defect of Eq. (22) is that for a binary electrolyte for which $|z_i| = z$, the resulting capacitance is symmetric under a change in the sign of the charge on the electrode. Allowing the ions to be of different size does not help much since the explicit solvent term dominates. Presumably, the asymmetry comes from the solvent. Effects such as a nonspherical solvent molecule, specific adsorption, and image forces should be uncoprorated into the model.

TABLE 1

Differential capacitance (f/m^2) in the limit of zero charge.
 (The theoretical values are for $\sigma=\sigma_d=2.76\text{\AA}$, $|z_i|=z=1$,
 $T=298\text{K}$, and $\epsilon=78.4$. The experimental values are for NaF.)

Core	Expt.	Theor. [Eq. (21)]
10^{-4}M	--	0.02
10^{-3}M	0.06	0.05
10^{-2}M	0.13	0.10
10^{-1}M	0.21	0.14
1M	0.26	0.16

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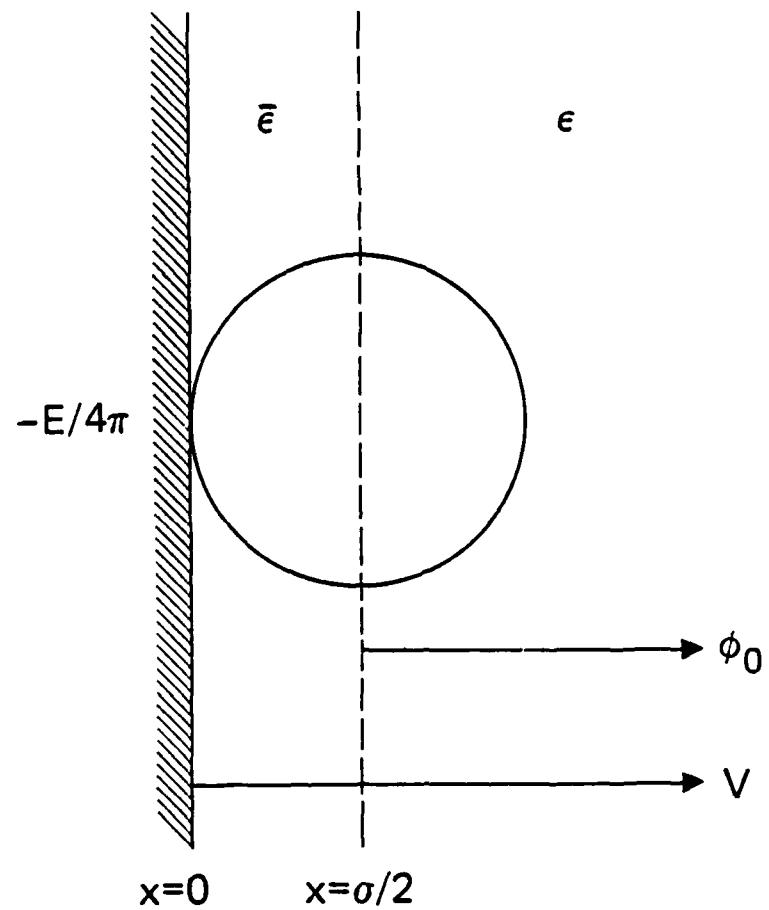


Figure 1. Double layer geometry in conventional inner layer treatment.

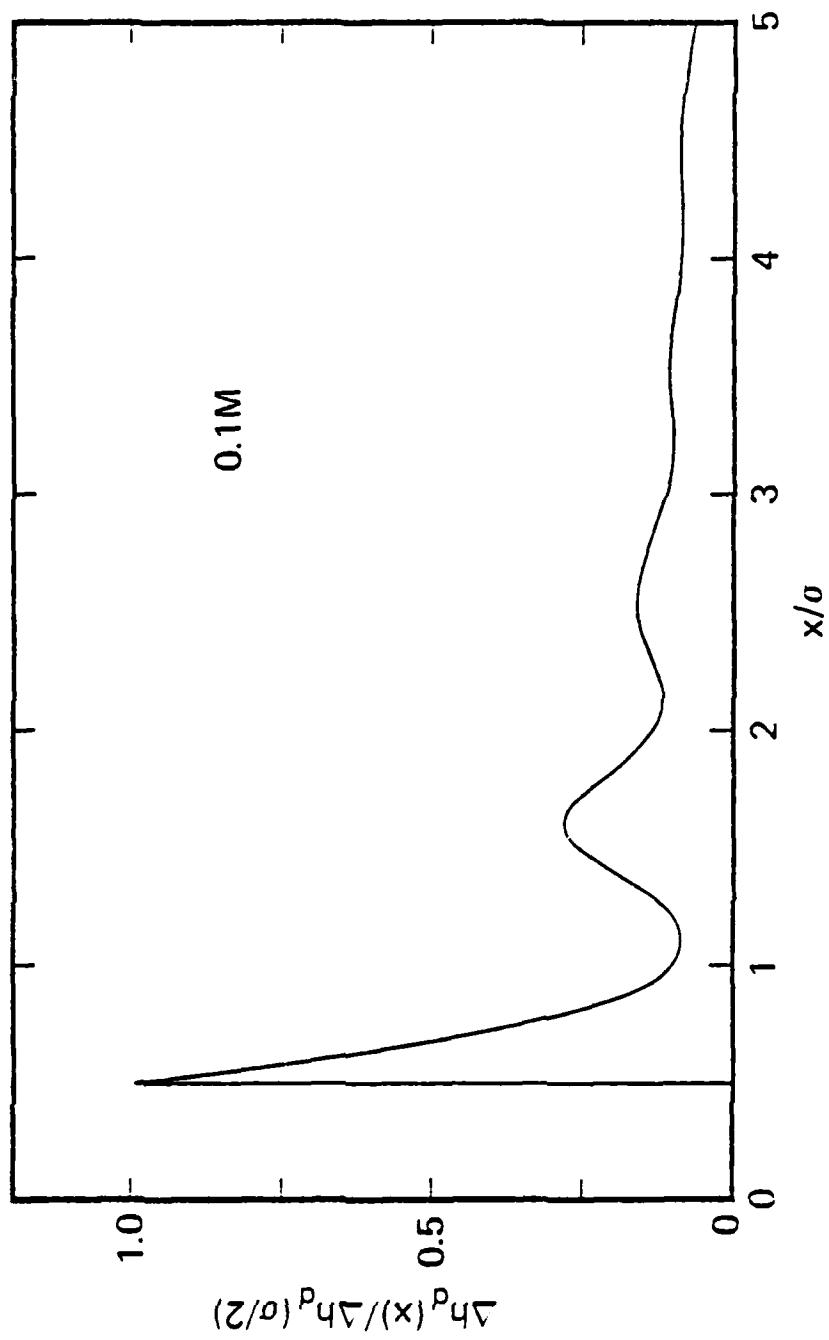


Figure 2. $\Delta\bar{\rho}_d(x)$ as a function of x in MSA for 10.1M solution ($|z_i| = z = 1$, $\sigma = \sigma_d = 2.76\text{\AA}$, $T = 298\text{K}$, and $\epsilon = 78.4$).

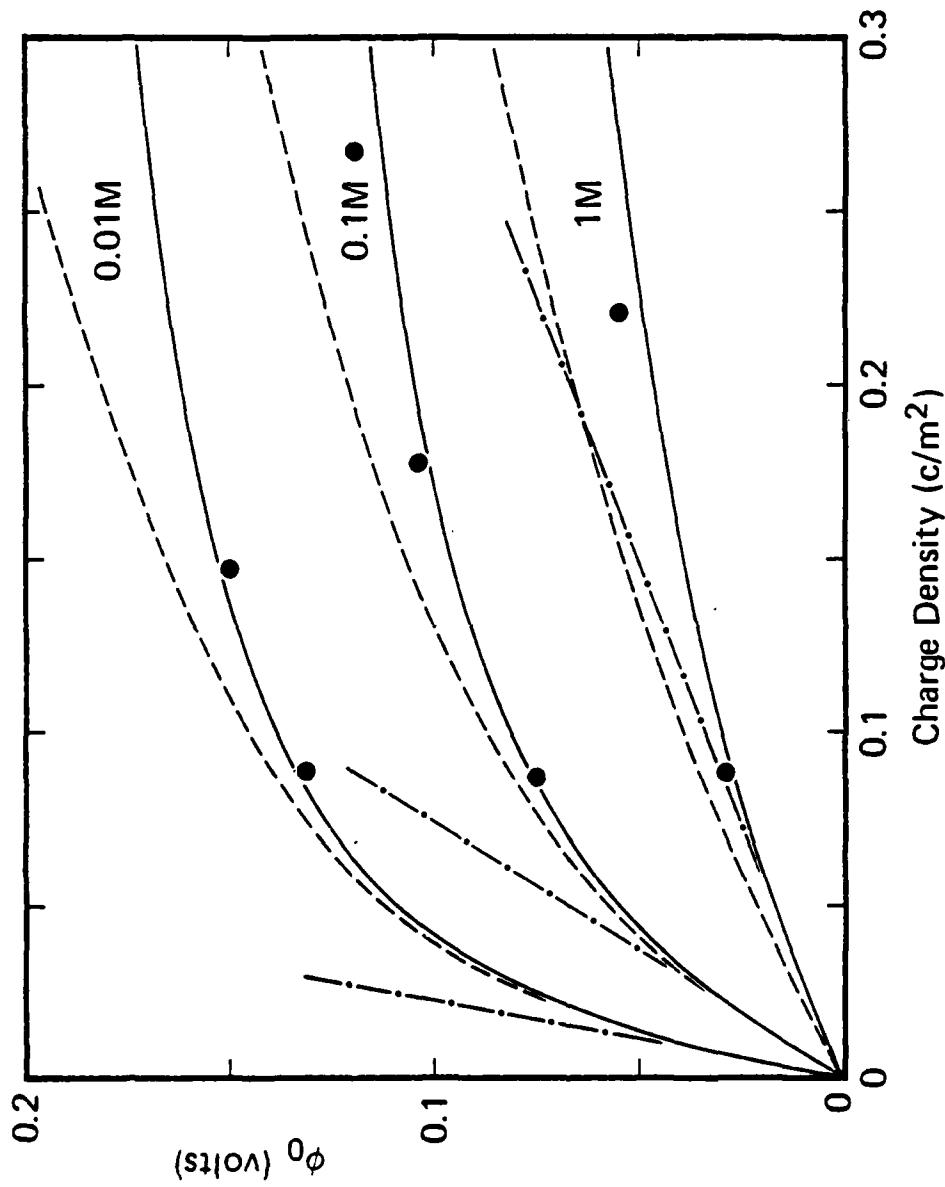


Figure 3. Diffuse layer potential as a function of the charge on the electrode for $|z_i| = z = 1$, $\sigma = 4.25\text{\AA}$, $T = 298\text{K}$, and $\epsilon = 78.5$. The points give the computer simulation results while the curves — — —, — · —, and — — give the GC, MSA, and HNC results, respectively.

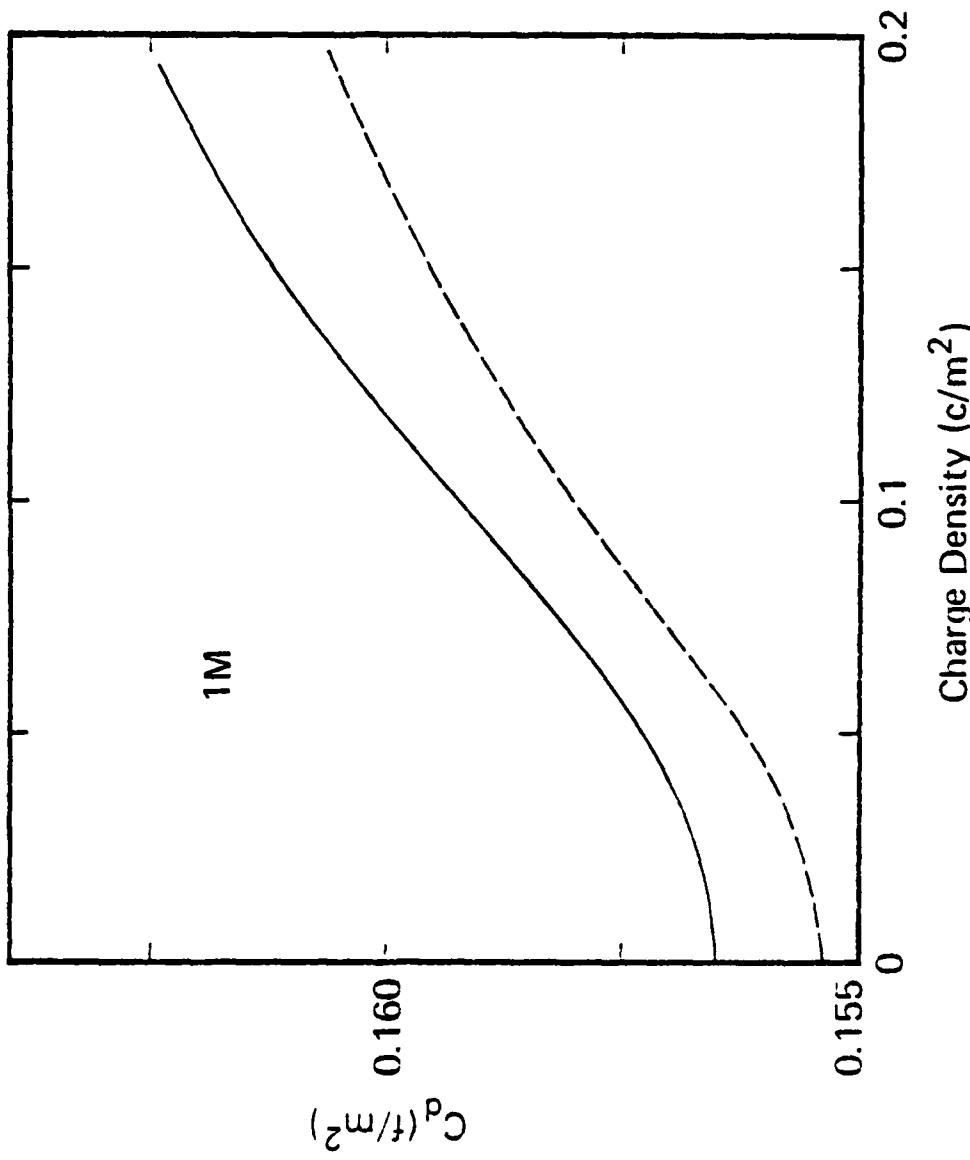


Figure 4. Differential capacitance as a function of the charge on the electrode for $|n_i| = z = 1$, $\sigma = 2.76\text{\AA}$, $T = 298\text{K}$, and $\epsilon = 78.4$. The solid and broken curves give the results of Eq. (22) using the HINC and GC theories, respectively, for $h_i(x)$.

